FT-IR Spectra of Soil Constituents: Fulvic Acid and Fulvic Acid Complex with Ferric Ions

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FT-IR spectra and corresponding second-derivative spectra, as well as pertinent difference spectra, of fulvic acid and of fulvic acid complexed with ferric ions have been obtained. The data reveal that the major functional groups present in the fulvic acid studied are carboxyl groupings and CH_2 groupings of hydrocarbon chains. The presence of ferric ions results in increased ionization of the COOH groups to form COO^- ions, as well as a change of the characteristic COO^- stretching frequencies of the carboxylate ions. The data thus indicate that ferric ions in soils interact with carboxylate ions of fulvic acids. The second-derivative spectra permit the identification of certain alkyl and aromatic hydrocarbon vibrational modes which cannot be observed in the original FT-IR spectra.

Index Headings: Fulvic acid; Iron-fulvic acid complex; Soil constituents; Infrared; Deconvolution; Second derivative.

INTRODUCTION

Fulvic acid (FA) is the organic soil component completely soluble in water at all pH values and conditions. FA is therefore the most suitable material for investigating important metal-organic interactions in soils.[1] Because of their ability to complex with mono- and multivalent metal ions, FAs are a particularly interesting class of soil components. The stability constants of metal-FA complexes are significantly lower than those for synthetic complexing agents (e.g., EDTA) and the same metal ion.[2] This observation suggests that metals complexed by FA should be more readily available to translocation and uptake by soil, plant, and microbial systems than is an ion sequestered by a synthetic compound. Infrared spectra of humic acids, fulvic acids, and their interaction products have provided much information regarding soil constituents over the years, information that was very difficult to obtain through other methods.[1,3,4] The acquisition of higher-quality spectra is now much more feasible with Fourier transform technology than it was with early dispersive instrumentation. Modern computer-facilitated techniques such as Fourier deconvolution, second-derivative spectroscopy, and spectral subtraction have been particularly useful in this context.[4] We have now applied some of these techniques to a more detailed investigation of complex formation between a previously described fulvic acid[1] and Fe^{3+} ions.

EXPERIMENTAL

The sample of fulvic acid (extracted from Armadale Bh horizon) and the preparation of the Fe^{3+} complex

have been previously described in detail.[1] The FT-IR spectra were obtained by the application of the KBr pellet technique and by the use of a Nicolet Model 7199 spectrometer operating at nominal resolutions of 4 and 2 cm^{-1}. The preparation of pellets has been described.[4] The spectrometer was equipped with a Globar source, a Ge/KBr beamsplitter, and a wide-range liquid-nitrogen-cooled Hg/Cd/Te (MCT) detector. The spectra were computed from 4000 signal-averaged scans. Each interferogram was phase corrected, once zero-filled, and apodized with the Happ-Genzel function. Second-derivative spectra were obtained from the observed absorbance spectra by the use of the function:[4,5]

$$A_n'' = (A_{n+1} - A_{n-1})/W^2 \qquad (1)$$

where A_n is the absorbance at point n, and W the wavenumber interval between data points n and $n + 1$. Difference spectra were obtained (1) by subtraction of the spectrum of the sample containing the complex from the spectrum of the original fulvic acid, so as to minimize the intensity of the 1600-cm^{-1} region COO^- asymmetric stretching band, and (2) by subtraction of the original fulvic acid spectrum from the spectrum of the complexed material, so as to minimize the 1700-cm^{-1} region C=O stretching band of the COOH groups. Although precise quantitative subtractions are not possible, because the sample concentration in KBr pellets is only approximately known, care was taken to avoid obvious distortions. Empirically we found that multiplying the intensity of the reference spectrum to be subtracted by 0.5 gave qualitatively satisfactory results. The exact band centers observed in the differential spectra are nevertheless less precise than the centers of the originally observed bands.

RESULTS AND DISCUSSION

Figure 1 shows the 3150-2650 cm^{-1} region of the FT-IR spectrum of fulvic acid (A) and the fulvic acid-Fe^{3+} complex (B), as well as the corresponding second-derivative spectra. Figure 2 shows the 1900-900 cm^{-1} region of these same spectra. Even with resolution enhancement, very little information pertinent to the main thrust of this paper could be gleaned from other spectral regions. These spectral regions are therefore not shown. One can immediately see that the major functional groups present in this sample are (1) protonated carboxyl groups, -COOH, with characteristic frequencies around 1700-1730 cm^{-1} (C=O stretching), as well as around 1400-1450 and 1200-1250 cm^{-1} (coupled C-O-H deformation and C-O stretching modes of the COOH group);[6-8] (2) car-
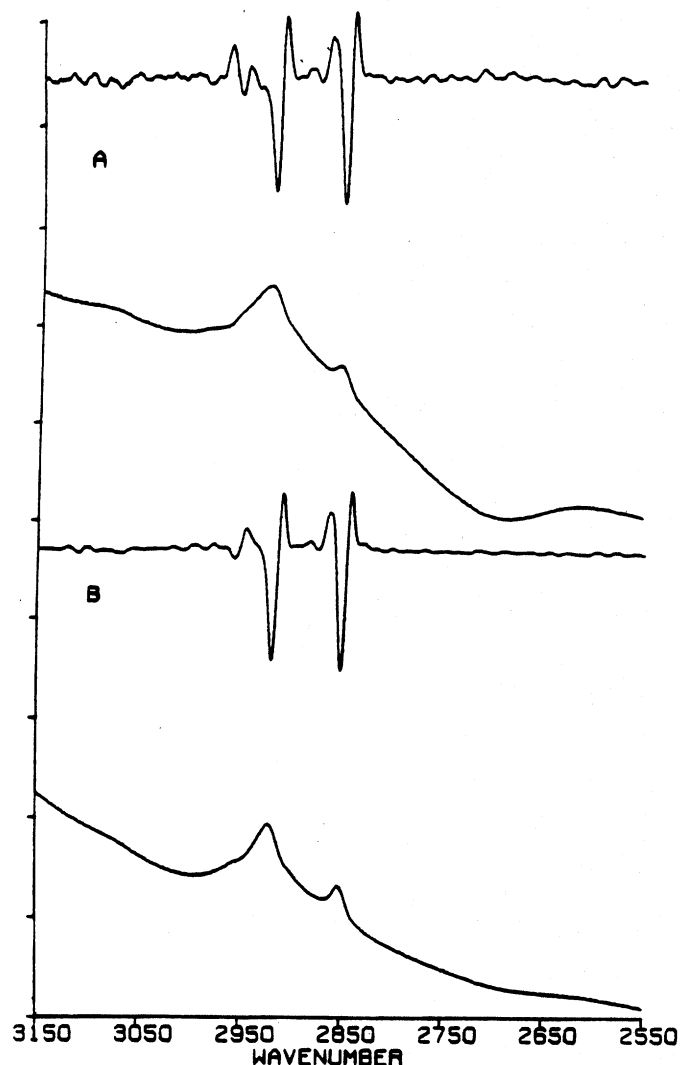
FIG. 1. Original FT-IR spectra [lower] and corresponding second-derivative spectra [upper] of fulvic acid (A) and of a fulvic acid/Fe^{+3} complex (B) [3150–2650 cm^{-1}]. The relative intensities (Y-axis) are in absorbance units for the original spectra and in units of absorbance/wavenumber^2 for the second-derivative spectra.

FIG. 2. Original FT-IR spectra [lower] and corresponding second-derivative spectra [upper] of fulvic acid (A) and of a fulvic acid/Fe^{+3} complex (B) [1900–900 cm^{-1}]. The relative intensities (Y-axis) are in absorbance units for the original spectra and in units of absorbance/wavenumber^2 for the second-derivative spectra.

boxylate ions, COO^-, with characteristic bands close to 1600 and 1400 cm^{-1}; and (3) aliphatic hydrocarbon groups exhibiting CH_2 stretching vibrations at 2921 (antisymmetric) and 2852 cm^{-1} (symmetric) and a CH_2 bending mode close to 1465 cm^{-1}.[4,6–8] By contrast, the previously investigated humic acid sample from Philadelphia city waste contained predominantly secondary amide groups, i.e., decomposition products of proteins.[4] FT-IR spectra can thus reveal, very rapidly, the predominant organic functional groups which comprise a given humic acid or fulvic acid sample. This fact is of paramount importance because both "fulvic acid" and "humic acid" are primarily procedural, not chemical, designations.[8]

Figure 2 also clearly reveals that while only the original spectra are needed in order for the COOH and/or COO^- groups to be observed, one must obtain second-derivative spectra to identify the characteristic methylene (CH_2) deformation band of hydrocarbon groupings, as well as those peaks associated with small numbers of aromatic rings and CH_3 groups, present in a given fulvic acid sample. Thus, we can now differentiate bands such as those
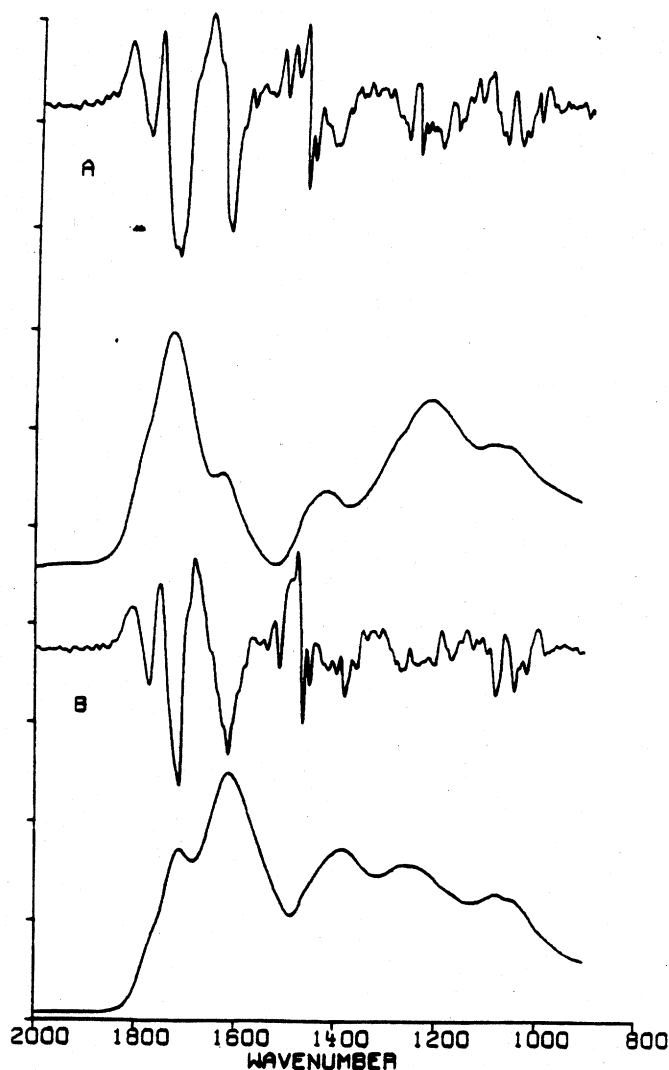
at 1515, 1494, 1468, 1455, 1416, 1400, and 1384 cm^{-1} which were not clearly distinguishable from routine FT-IR spectra (Table I, Fig. 2).

The effect of complex formation with Fe^{3+}, as seen in Fig. 2B, is twofold. The number of COO^- groups is increased, as indicated by the increased intensities of the bands in the 1600- and 1400-cm^{-1} regions, and the frequencies of the COO^- stretching modes are decreased, as shown in Table I. The equilibrium:

$$R\text{-COOH} \rightleftharpoons R\text{-COO}^-$$
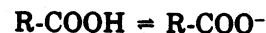
is thus shifted to the right, while at the same time the stretching frequencies of the carboxylate ion are slightly altered. Also of interest is the observation that the frequencies of both COO^- stretching modes appear to decrease slightly upon complex formation with Fe^{3+}. This observation suggests that the affinity of the Fe^{3+} ions for the carboxylate groups is less than that typically observed for simple, metal carboxylato complexes.[2]

Table I summarizes the observed frequencies of the original fulvic acid, fulvic acid complexed with Fe^{3+} ions,

TABLE I. Observed frequencies (cm⁻¹) of the original fulvic acid (FA), of the FA complex with Fe^{3+}, and of difference spectra.

Assignment[a]	FA (A)	FA/Fe³⁺ (B)	Difference spectra:[b]	
			(B − 0.5A)	(A − 0.5B)
OH str		3400[c]	3400[c]	
CH₂ asym str		2921	2921	
CH₂ sym str		2852	2852	
Fermi resonance component?	}	1782	1773	
C=O of COOH	1723	1713	···	1728
COO⁻ sym str	1622	1615	1603	(1626)[d]
Ar ring str	1515[e]	1515[e]		
Ar ring str	1494[e]			
CH₂ scissor	1468[e]	1467[e]		
Ar ring str; CH₃ asym def?	}	1455[e]	1455[e]	
COH def of COOH	1416[e]	1412[e]		1416[c]
COO⁻ asym str	1409	1385	1381[c]	
CH₃ sym def?	1384[e]			
C-O str of COOH;	1288[e]	1272[e]		
COH bend of phenols	1235[e]	1246[e]		
and 3° alcohols;	1205[e]	1204[e]	···	1206[c]
C-O str of Ar-OR	1169[e]	1173[e]		
C-O-H bend, alcohols	1078	1080		
	1044 sh	1045 sh		

[a] Abbreviations: Ar = aromatic; R = alkyl; sh = shoulder; str = stretch; def = deformation; sym = symmetric; asym = antisymmetric.
[b] Approximate values for carboxyl and carboxylate bands only.
[c] Approximate value of very broad band.
[d] Very weak.
[e] From second-derivative spectra.

FIG. 3. Difference spectra in the 2000–800 cm⁻¹ region. Left: A − 0.5B. Right: B − 0.5A. A and B as in Figs. 1 and 2.

and frequencies of pertinent difference spectra. Some uncertainty is apparent in the 1390–1450 cm⁻¹ region, where one of the COOH deformation modes overlaps with the symmetric COO⁻ stretching mode.[6,7] The second-derivative spectra suggest that the COOH deformation mode centers around 1415 cm⁻¹ (weakened by complex formation), while the COO⁻ stretching mode centers close to 1400 cm⁻¹ (intensity increased, frequency decreased by complex formation).

Figure 3 presents difference spectra in the carboxyl region which confirm the previous conclusions. Figure 3A shows strong bands characteristic of protonated COOH groups. The strong asymmetric COO⁻ stretching band in the 1600-cm⁻¹ region has been reduced to a very weak shoulder. Figure 3B presents the carboxyl region of the Fe³⁺ complex. Strong bands are observed close to 1605 and 1380 cm⁻¹ (asymmetric and symmetric COO⁻ stretching modes), while the COOH bands in the 1725-cm⁻¹ and the 1200-cm⁻¹ regions have virtually disap-

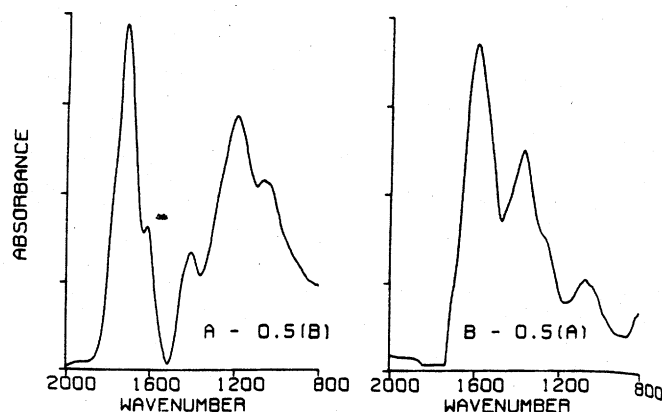peared. As mentioned above, the band centers of the difference spectra are somewhat uncertain because of the imprecision introduced in subtracting spectra obtained by the KBr technique. The data nevertheless clearly demonstrate (1) that the ferric ions are substantially increasing the ionization of the carboxyl groups and (2) that interaction with ferric ions influences the frequencies of the carboxylate ions. One may therefore conclude that, in soil samples with high levels of ferric ions, interactions with the carboxylate ions of fulvic acid should be important.

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